Granular metal films as recording media

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High-density recording media require materials with a high magnetization and high coercivity as well as chemical stability, wear, and corrosion resistance. We explore the potential of granular metal films for recording media. Films of Fe granules about 150 Å in size embedded in an amorphous SiO_2 matrix exhibit coercivities as high as 3 kOe at low temperatures and 1.1 kOe at room temperature, and magnetizations of about 150 emu/g. The methods with which these materials are fabricated, the essential microstructure characterization, and magnetic measurements are described.

Today, vast amounts of audio, video, and digital information are stored in magnetic tapes and disks. The demand for high-density recording media with superior magnetic characteristics is ever increasing.[1] Suitable media for technological applications must also be chemically stable and wear resistant. Magnetic granular solids[2] (e.g., $Fe-SiO_2$), in which ultrafine magnetic particles (with sizes 20–300 Å) are embedded in an insulating matrix, offer attractive features as recording media. First of all, the superior magnetic properties of the granular solids are microstructure controlled and can be tailored through process conditions. The insulating matrix (e.g., SiO_2, Al_2O_3) greatly enhances the chemical stability of the magnetic particles, and the wear and corrosion resistance of the media. Furthermore, since vapor deposition is the most effective method of making granular metal films, the fabrication, dispersion, and protection of the ultrafine granules, as well as coating onto desired surfaces suitable for device applications, are achieved in a single process.

In granular metal films, the microstructure is crucial to the unusual magnetic properties. The size and shape of the metal granules, their connectivity, and the associated percolation behavior are of primary importance. We have recently found in granular $Fe-SiO_2$ that when the metal volume fraction (p) is near the percolation threshold (p_c), greatly enhanced magnetic properties are realized.[3] As shown in Fig. 1, the coercivity (H_c) at low temperatures was found to be as high as 2500 Oe, two order of magnitude higher than that of bulk Fe. However, these samples have been deposited onto room-temperature substrates, where the metal granules are relatively small (≤ 70 Å). Consequently, H_c at room temperature is much reduced, primarily because of superparamagnetic relaxation. Fortunately, the magnetic properties can be further improved by altering the process conditions, particularly the substrate temperature.

In this work we demonstrate Fe granular films fabricated at different conditions with room-temperature coercivity as high as 1125 Oe. Equally important, a magnetization of 150 emu/g (which is about twice of those of $\gamma-Fe_2O_3$ and Co-Cr) has also been achieved.[4,5] These characteristics compare very favorably with many existing media for magnetic recording. The relationship between these superior magnetic properties and microstructure will also be discussed.

The granular $Fe-(SiO_2)$ films have been prepared by a high-rate rf magnetron sputtering device with the use of composite targets of Fe and SiO_2. All samples, except those for transmission electron microscopy (TEM), are about 2–5 μm in thickness, deposited onto various substrates (glass, mica, Kapton, metals, alumina, etc.) suitable for specific measurements. Very good adhesion to Kapton, glass, and metal substrates has been noted. Sputter deposition has been made with substrates at various temperatures (77–875 K) in order to alter the morphology of the films. The microstructure and composition of the samples have been characterized by TEM, electron, and x-ray diffractions, atomic absorption, and ^{57}Fe Mössbauer spectroscopy. The magnetic properties have been measured by a SQUID magnetometer with a field range of 0–50 kOe and temperature range of 2–400 K.

The composition of $Fe_{75}(SiO_2)_{25}$ with $p = 0.42$ was chosen because a maximum in H_c was achieved, as shown in Fig. 1. A number of process conditions, such as sputtering gas pressure, deposition rate, and substrate temperature, were varied in order to fabricate samples with different microstructure, particularly larger granule size. This is moti-
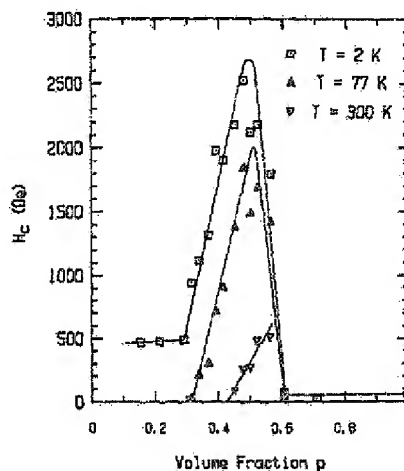

FIG. 1. Magnetic coercivities ($T = 2$, 77, and 300 K) of granular $Fe-SiO_2$ films deposited onto room-temperature substrates as a function of Fe volume fraction (Ref. 3).
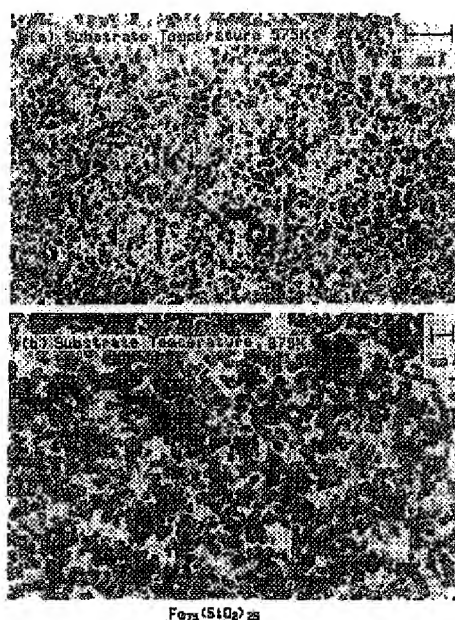
FIG. 2. TEM micrographs of Fe_{75} (SiO_2)$_{25}$, $p = 0.42$, about 500 Å thick, sputtered at substrate temperatures of (a) 575 K and (b) 875 K.

FIG. 3. X-ray diffraction pattern of Fe_{75} (SiO_2)$_{25}$, $p = 0.42$, deposited at T_s = 77.6 K. The expected pattern for bulk α-Fe is also shown.

vated by the fact that the superparamagnetic relaxation rate depends sensitively on the particle size through the factor $\exp(KV/k_BT)$, where K is the magnetic anisotropy energy per volume and V is the particle volume.[6] Even a modest increase of V (e.g., a factor of 2) should drastically alter the temperature dependence of the magnetic properties. Of the above-mentioned process conditions, substrate temperature has the most pronounced effect.

The granular nature of the Fe-SiO$_2$ samples with $p = 0.42$ deposited onto substrates at substrate temperatures (T_s) between 77 and 875 K is revealed by TEM. For samples deposited between 77 and 400 K, the granules are about 40 Å and do not vary significantly in size. As shown in Fig. 2(a), the sample deposited at $T_s = 575$ K contains larger granules of about 60 Å. The size of the granules can be greatly increased with higher T_s. As shown in Fig. 2(b), in the films deposited at $T_s = 875$ K the granule size is about 160 Å. Above 400 K, the size of the granules increases by about 25 Å per 100 K. The x-ray diffraction pattern of a film deposited at 77.6 K is shown in Fig. 3. The pattern can be consistently indexed to the structure of bcc Fe with a broad background contribution from amorphous SiO_2. However, we note that the (110) peak at 45° is slightly asymmetrical. The possibility of other phases of Fe is being investigated. We have also used ^{57}Fe Mössbauer spectroscopy to probe microscopically the Fe-containing portions of the samples. The spectra exhibit essentially the same hyperfine field as that of α-Fe, although the linewidths are noticeably broader, as expected from the small granules. There are no observable amounts of Fe oxides, which would generally exhibit much larger hyperfine fields. These analyses indicate that the granules are primarily pure Fe.

From the value of 155 emu/g of total sample material for the saturation magnetization, measured at 6 K, one ob-
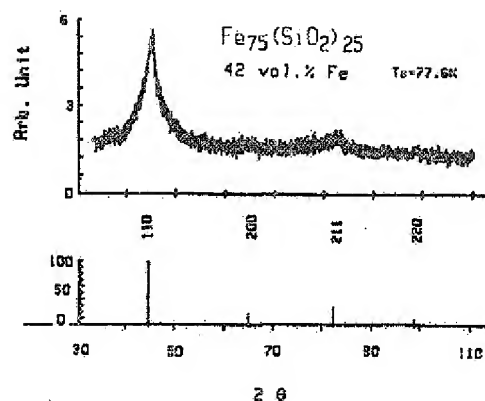
tains a value of 210 emu/g of Fe, which is within 5% of the value for pure Fe. The magnetic moment per Fe is therefore about $2\mu_B$. There is no evidence of enhancement or diminution of the Fe moment.

By increasing the granule size, as facilitated by higher T_s, the coercivity is dramatically affected in both magnitude and temperature dependence. As shown in Fig. 4(a), H_c at 6 K increases from 1.5 kOe to about 3 kOe as T_s is increased from 300 to 775 K. These values at 6 K are essentially those of the ground state. The values of H_c at 300 K are considerably reduced as expected, but the reductions are not proportional to the values at 6 K. This is because the temperature dependence of H_c is largely dictated by the granule size; the more pronounced temperature dependence occurring in the smaller granules. Consequently, for the smaller granules (T_s < 475 K), H_c is essentially zero at 300 K. On the other hand, for samples with $T_s > 800$ K, H_c at both 6 and 300 K also decreases precipitously. There are two likely causes. The granule sizes for these samples are about 150 Å, approaching the estimated critical size of 200 Å for single-domain Fe particles. Some granules may become multidomain, which drastically degrades H_c. A more likely cause, however, is the alteration of the granular structure at high temperatures. The TEM micrograph shown in Fig. 2(b) indicates sintering between the granules. The partially connected granules effectively allow the formation of multidomain, thus reducing H_c.

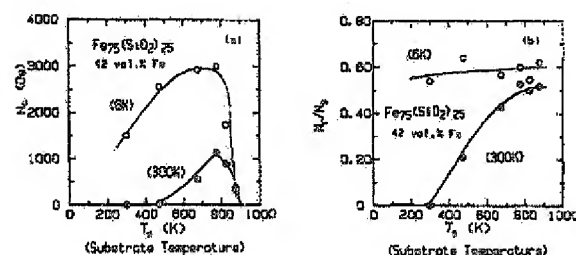A maximum of H_c at both 6 and 300 K is achieved with

FIG. 4. Variations of (a) coercivity and (b) squareness of Fe_{75} (SiO_2)$_{25}$, $p = 0.42$, at 6 and 300 K as a function of substrate temperatures.

$T_s = 775$ K. The values of H_c of 3 kOe (at 6 K) and 1.1 kOe (at 300 K) are among the highest for Fe particles. The high value at 300 K is particularly encouraging for possible recording media applications.

In Fig. 4(b) we show the squareness, defined as the ratio of remanence and saturation magnetization. The squareness at 6 K is about 0.6, essentially independent of T_s. As expected, the squareness at 300 K is reduced, but the reduction is much more for the smaller particles for the same reasons mentioned earlier. The squareness at 300 K is also the highest for $T_s > 775$ K, as in the case of H_c.

Finally, we should mention some possible causes for the giant coercivity. It is well known that for single-domain equiaxial Fe particles, H_c is of the order of $2K/M$, where K includes all contributions (magnetocrystalline, stress, surface, etc.) to the magnetic anisotropy. Since magnetization (M) is essentially independent of particle size, a larger H_c would necessarily mean K scales with the particle size in the present case. If one makes the overly simplistic assumption that magnetocrystalline anisotropy is the only contribution and that its magnitude is the same as that of bulk Fe, one concludes that H_c should be only about 600 Oe and independent of particle size.[6,7] It is clear then that some contributions, particularly those due to surface and stress, may well acquire much enhanced values, because the Fe granules are not free standing, but bonded in the SiO_2 matrix. Other pos-sible causes for the enhanced H_c are particles with large aspect ratio or particles forming very long chains. Neither of these possibilities are revealed in TEM micrographs, although there are evidences of neighboring granules in contact.

In summary, by exploiting granular Fe-SiO_2 solids with large granular sizes (about 150 Å), we have achieved room-temperature coercivity of 1.1 kOe and magnetization of 150 emu/g. These materials may be produced by sputtering with the use of suitable process conditions, of which substrate temperature is the most important. These superior magnetic characteristics compare favorably with those of existing magnetic recording media. The deposition methods, with which granular magnetic solids are made, are particularly suitable for magnetic thin-film applications.

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